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Pulse Electrodeposition of Sn-Ni-Fe Alloys and Deposit Characterisation for Li-ion Battery Electrode Applications

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Abstract: Characterisation of Sn-Ni-Fe ternary alloy deposits obtained by pulse electrodeposition show that novel alloys of varying composition can be successfully deposited exhibiting amorphous structures using specific on/off pulse plating parameters for electrodeposition in combination with an electrolyte based on gluconate as a complexing agent. The deposits obtained exhibited high quality bright metallic surface morphologies combined with a distinct pronounced spherical/nodular grain structure across a range of average current densities. The influence of on/off period pulse current and the effect of the average current density on the surface morphology of the electrodeposited films were studied using Scanning Electron Microscopy (SEM). The cathode efficiency results obtained show that the pulse electrodeposition process chosen is significantly more efficient than the constant current electrodeposition. Results suggest that the substrate surface deformation condition and preparation are critically important in achieving a surface morphology suitable for an effective Sn-Ni-Fe alloy battery electrode. The alloy deposits with a morphology, which exhibits a high surface area per unit volume, are shown to be promising as an alternative anode material for lithium ion batteries.

Keywords: Pulse Electrodeposition, Amorphous Alloys, Sn-Ni-Fe Ternary Alloys, Thin Films, SEM, Li-ion Battery Electrodes, Substrate Surface Condition

1. Introduction

Li-ion batteries are one of the most important electrochemical power sources used to satisfy our existing and future energy needs. Substantial effort and investment are being directed toward accelerating the development of practical hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs), energy-efficient cargo ships, rail power, aerospace, power-grid applications and stationary storage of renewable energies such as solar and wind [1-3]. The Li-ion battery industry employs a wide variety of metals, metallic alloys and non-metallic materials with different structures as electrodes in various types of batteries. However, high cost, safety concerns, and the limited capacity of the graphite anodes (theoretical capacity of 372 mAh/g) demand the development of alternative materials for the next generation of energy storage devices [4, 5]. Tin-based alloys have attracted considerable interest as a more efficient alternative to pure tin anodes and traditional graphite based materials for Lithium-ion batteries. Tin has a higher specific

theoretical capacity of 990 mAh/g [6] and currently appears to be one of the most promising candidates to replace graphite anode in lithium ion batteries.

Pulse electrodeposition methods have been extensively employed to obtain co-deposition of iron group alloys such as Fe-Ni [7-11] and to obtain good quality tin electrodeposition [12]. Pulse plating methods have also been shown to improve essential factors such as the electrodeposited surface morphology, the microstructure, appearance, corrosion resistance, hardness, residual stress and magnetization of iron-group alloy coatings compared to that achieved by using direct current techniques [7-11, 13, 14].

Amorphous alloy materials reported to show homogenous volume expansion during lithium insertion with no pulverization and high cycleability [15-19]. In earlier papers, the present authors [20, 21] reported that the pulse electrodeposition is an efficient method to deposit Sn-Ni-Fe ternary alloys exhibiting predominantly amorphous structures. Various pulse parameters were studied in order to determine their effect on the microstructure employing Conversion Electron Mossbauer Spectroscopy (CEMS) and X-ray

Diffraction. The results revealed that different on-time pulse currents facilitate the formation of a ferromagnetic or paramagnetic phase in the Sn-Ni-Fe alloy. The performance and the capacity of different samples as an anode in a Li-ion battery have been studied. [20].

The objective of the research studies reported in this paper is to extend the earlier results for electrodeposited Sn-Ni-Fe alloys [20, 22, 23] and discuss the characterisation of the surface morphology of the deposits, examine the effect of the Cu substrate surface condition on deposit morphology and report on the electrode performance of Sn-Ni-Fe alloy electrodeposits using specific on/off pulse electrodeposition conditions to achieve alloys with enhanced potential as an alternative anode materials for improved Li-ion batteries.

2. Materials and Methods

Copper substrate (as cold-rolled 99.97% purity, 0.175 mm thickness) test coupons with dimensions 5×1 cm were used with an electroplated area of 2×1 cm on either side. The coupons were degreased using acetone and prepared for electrodeposition as follows;

(1) used with additional electropolishing in phosphoric acid solution (66 wt. %) at a constant current of 0.25A/cm² for 2 minutes and thereafter rinsed in deionised water immediately prior to electrodeposition;

(2) used with additional immersing into the electropolishing solution for 30s in order to remove any residual grease of the manufacturing process and thereafter rinsed in deionised water immediately prior to electrodeposition;

(3) used with additional grinding operations applying Grade 1200 sandpaper for 30s to increase the surface area per unit volume and then rinsed in deionised water immediately prior to electrodeposition.

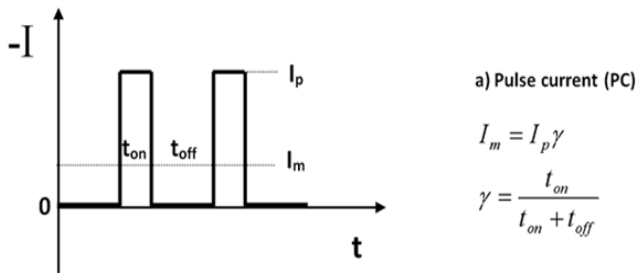


Figure 1. The square-wave pulse signal main parameters.

The electrolyte was prepared using an aqueous solution containing 0.3M NaCl, 0.3M H₃BO₃, 0.02M SnSO₄, 0.05M NiSO₄, 0.02M FeSO₄, 0.2M Sodium gluconate with 2g/l concentration of ascorbic acid used as an antioxidant and 0.1g/l peptone as a surfactant. The electrodeposition was carried out in a glass cylindrical cell at 20°C using a pH of 6.0 and agitation in combination with the use of different specific pulse current parameters which are described in Table 1. Fig1 illustrates the notations of the square-wave pulse signal parameters used. The cell anodes consisted of high density carbon, situated at 1 cm distance on either side of the copper cathode such that both sides of the cathode could be

electroplated under similar current distribution conditions. Typically, three identical test samples were prepared for each set of deposition conditions.

The surface morphology was observed with a Zeiss EVO 50 scanning electron microscope and the elemental composition was determined using an EDAX EDS detector at 20kV and I_{beam}=40pA.

A model Li-ion cell was used for testing the electrochemical performance. Lithium metal foils were used as the reference and counter electrodes. There was no separator in the cell. The electrolyte was 1M LiClO₄ dissolved in Ethylene Carbonate: Dimethyl Carbonate (1:1 by volume) solution. The cells were assembled in a glove box filled and purged with argon gas to maintain the environment at less than 10 ppm of water. Cells were cycled at 20°C between 0.02V and 1.5V versus Li/Li⁺ at a constant current rate of 0.2C, which can be calculated from the tin content using (1):

$$I_{cycling} = \text{Sn}_{theoreticalcapacity} * \text{Sn}_{wt\%} * C_{rate} * \Delta m \quad (1)$$

3. Results and Discussion

Table1 show typical results obtained using pulse deposition parameters alongside a typical result for constant current deposition (deposit 1). It can be seen for electrodeposits 3 to 6 obtained using t_{on}=0.01s and t_{off}=0.49s that the increase in the average current density causes the Fe content to decrease by about 16wt%, the Ni content to fluctuate around an average of 6 wt% and the Sn content to increase by about 15wt%. Higher Sn contents are important to ensure the specific theoretical capacity is as near to the 990mAh/g as possible while at the same time ensuring that significant amounts of Ni and Fe are present to provide alloying which it was hoped would stabilise and minimise volume changes of the electrodeposited electrode during the lithiation-delithiation cycles which occur during the operational functioning of the Li-ion battery cell. By comparing electrodeposits 1 and 2 it can be seen that employing pulse electrodeposition (t_{on}=0.1s) leads to a significant increase in the Sn content of the alloy of around 13wt% compared to constant current deposition.

The current efficiency for the constant current deposition and the pulse plating using t_{on}=0.1s, t_{off}=0.9s was found to be very similar at around 29% and 26%, respectively, but for the electrodeposits obtained using t_{on}=0.01s, t_{off}=0.49s the current efficiency shows a decrease with increasing I_p and I_m from a very high value of around 95% for deposit 3 to a very low value of around 4% for deposit 6. This is due to the progressive increase in hydrogen reduction at the cathode with metallic nucleation and growth at the cathode surface being inhibited due to changes in the deposition kinetics, thus hindering the adsorption of the plating additives on to the cathode surface during deposition and resulting in an increased grain size. Hydrogen evolution may also increase mass transport and encourage grain growth rather than fresh nucleation leading to the corresponding compositional changes observed in the deposited alloys shown in Table 1. These changes to the nucleation and growth of the

electrodeposits on the cathode are most probably also associated with changes to the surface morphologies of the final alloy deposits which could significantly affect the required properties of the electrode deposits being tested as an electrode in the Li-ion cell.

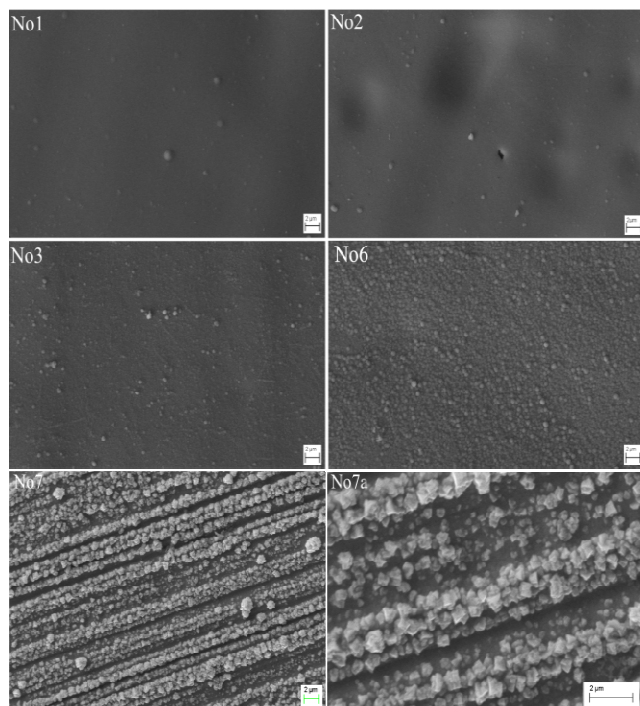


Figure 2. Surface morphology of the selected samples using SEM.

Fig2 shows typical SEM micrographs (magnification $\times 10,000$) of the surface morphologies obtained for the pulse electrodeposited Sn-Ni-Fe alloys. In general the deposits exhibited surface morphologies which were compact and bright metallic in nature, had a fine grain distribution and were free of porosity and any form of surface cracking. The SEM micrographs show the influence on the surface morphology of the pulse current duty ratio (t_{on}/t_{off}) as well as the pulse current parameters (I_p and I_m). No significant differences in surface morphology are evident in the electrodeposits obtained at constant current deposition (deposit 1) and pulse electrodeposition (deposit 2). The similarity found for the microstructures is consistent with their deposition current efficiency being similar in value at current densities $7.27\text{mA}/\text{cm}^2$ and $6.99\text{mA}/\text{cm}^2$. Deposit 3, obtained using $t_{on}=0.01\text{s}$, shows the initiation of a more distinctive spherical particle growth which probably correlates to the effect of a hundredfold decrease in the pulse time which in turn probably stimulates further spherical grain nucleation and subsequent growth. Comparing deposits 3 and 6, it can be seen that the fine particle size (average diameter of around 100nm) observed for deposit 3 changes with increasing average current density to give greater amounts of the more pronounced spherical/nodular particle distribution whereas for deposit 6 the average diameter of the particles was about 300nm . The change in growth is most probably due to the increased current density resulting change in the deposition

kinetics at the diffusion layer leading to a more pronounced spherical/nodular grain structure.

Changing the substrate surface morphology prior to the alloy deposition process significantly changes the nucleation kinetics of the Sn-Ni-Fe alloy deposition process. The as cold-rolled copper foil surface for electrodeposit 7 was rinsed in the electropolishing solution to simply remove any residual grease and other detritus deriving from the prior industrial handling process. Pulse electrodeposition was then conducted on the as cold-rolled clean Cu foil substrate using $t_{on}=0.01\text{s}$ and $t_{off}=0.19\text{s}$, and as can be seen alloy deposit 7 exhibits a significantly different morphology from the other samples shown in Fig2. Nucleation and subsequent growth has provided a much more pronounced spherical/nodular structure which is preferentially aligned with the deformation lines relating to what is probably the original direction of the industrial rolling process used to produce the Cu foil being used as the substrate material for the electrodeposition studies. The preferential growth alignment is most probably due to the observed variation in the nature of the cathode surface where nucleation and subsequent growth has clearly developed along the residual high surface energy deformation lines. As can be seen from Fig2 the SEM photomicrograph of deposit 7a, which is a higher magnification ($\times 30,000$) of deposit 7, reveals the highly deformed micro-surface has yielded a surface structure with a large surface area per unit volume ratio which is more nodular than spherical in shape but nevertheless is a highly desirable deposit for the provision of a higher exchange current rate in Li-ion battery technology [24].

It appears that the formation of a more pronounced nodular particle distribution is facilitated by applying the short pulse time deposition ($t_{on}=0.01\text{s}$) compared to the long pulse time deposition ($t_{on}=0.1\text{s}$). Where $t_{on}=0.01\text{s}$, the much shorter pulse deposition time probably stimulates greater nucleation of the alloy at the cathode with each pulse cycle thus generating a large number of growth centres leading to a more nodular particle distribution. This difference is not surprising as conditions at the catholyte-electrode interface could be expected to be significantly different with a tenfold difference in the on-pulse time. With higher current density, hydrogen obviously competes for reduction at the cathode as shown by a decreasing efficiency with increase in pulse current (I_p). This may also contribute to the nucleation of the more pronounced nodular grain structure. The increase of the peak current (I_p) causes the average diameter of the nodular particles to increase up to 300nm for deposit 6 where the peak current (I_p) has increased by a factor of four. The more pronounced nodular particle distribution generated using $t_{on}=0.01\text{s}$ would thus tend to have a much greater surface area which would be an attractive surface morphology for an electrode in Li-ion batteries [24].

Previously reported results [20] with regards to Sn-Ni-Fe electrodeposits, galvanostatic charge-discharge test results, with similar alloy compositions to those reported for deposits 3 and 7 in Table1, are shown in Fig3. In this paper, these initial results are reproduced and extended. The earlier results showed [20], that the capacity after the 1st cycle for an alloy

deposit with 62 wt% of Sn gave a value of 530mAh/g with a charge-discharge efficiency of 89%. For an alloy deposit of 82 wt% of Sn, the capacity after the 1st cycle was 755mAh/g with

a charge-discharge efficiency of 95%. It was found that after 10 cycles the discharge capacity remained constant.

Table 1. Pulse deposition parameters and corresponding composition of Sn-Ni-Fe alloy deposits.

No.	Deposition parameters					Elemental composition			Current efficiency (%)
	t_{on} (s)	t_{off} (s)	I_p (mA)	$I_m/Area$ (mA/cm ²)	Duration (s)	Sn Wt%	Ni Wt%	Fe Wt%	
1	1	0	-10	-7.27	600	50.1	12.9	37.0	29.4
2	0.1	0.9	-100	-6.99	600	63.0	7.0	30.0	26.7
3	0.01	0.49	-100	-1.67	600	63.0	6.5	30.5	95.4
4	0.01	0.49	-200	-5.00	600	78.8	7.4	13.8	49.2
5	0.01	0.49	-300	-6.00	600	79.7	5.4	14.9	23.3
6	0.01	0.49	-400	-8.00	600	81.2	4.8	14.0	4.3
7	0.01	0.19	-100	-2.94	900	82.4	3.1	14.5	97.0

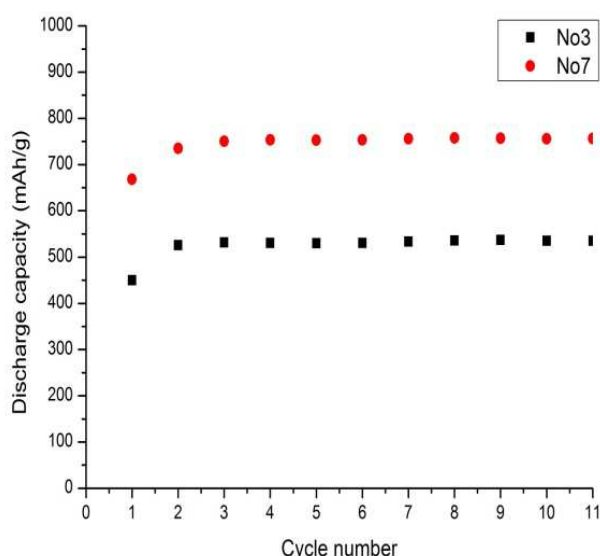


Figure 3. Galvanostatic charge-discharge tests of Sn-Ni-Fe samples as published earlier [20].

Compared with the carbon anodes, which have an average discharge capacity of 320mAh/g, these initial results suggested that pulse plated Sn-Ni-Fe deposits could give a two times higher specific capacity with a sustainable cycle life compared to carbon electrodes

Further studies were conducted to elucidate the role of the Cu surface substrate condition with regards to achieving deposits which showed good quality electrode properties for the Li-ion cell. From initial results it appeared that directional surface deformation could deliver deposits with a surface morphology which exhibited a high surface area per unit volume that is desirable for the electrode properties for Li-ion cells. On this basis various Cu substrate preparation methods were tested and the resulting deposits obtained were then measured in the model lithium cell using a series of similar Sn-Ni-Fe deposits in composition to deposit 3 (62Wt% of Sn) shown in Table1 and these results are shown in Fig4. The surface morphology of the as-rolled Cu foil substrate prepared by 2 minutes electropolishing resulted in a highly smooth surface which exhibited a high specular reflectivity and as can be seen from Fig4, this form of substrate surface preparation did not seem to facilitate the desired deposited structure as the

charge-discharge cycle test resulted in a poor discharge capacity in conjunction with significantly poor cycleability for the deposited alloy electrode. It was anticipated that the addition of directional deformation marks to the electropolished surface to simulate the deformation obtained during the manufacture of the Cu foil would improve the electrode properties.

However, as can be seen in Fig4, the deposited electrode performance showed no improvement in properties when compared with the electropolished substrate. This may be due to the electropolishing process producing such a smooth surface that the deformation marks had little effect compared to the original deformation resulting from manufacture of the Cu foil which had probably been completely removed by electropolishing.

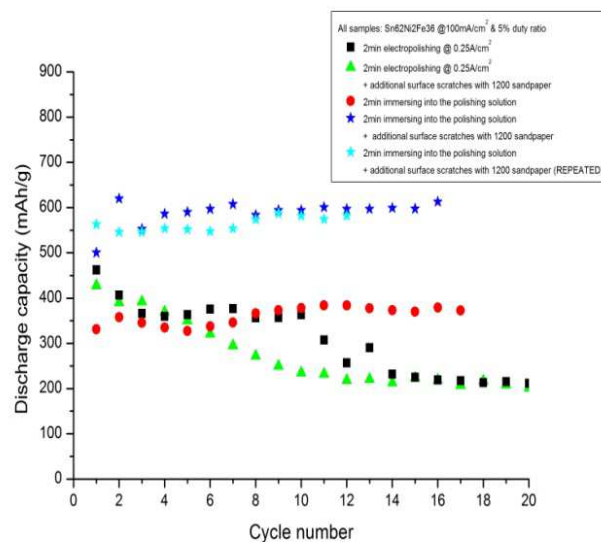


Figure 4. Galvanostatic charge-discharge tests and cycling efficiency of Sn-Ni-Fe samples with different substrate surface treatment (reproduced deposit 3 samples).

This suggested that it was important to retain the surface condition of the as manufactured copper foil which exhibited an aligned highly deformed micro-surface which only required immersion cleaning in the electropolishing solution to remove the organic contamination (grease) and other detritus associated with foil manufacture. The surface morphologies for the electropolished and immersion cleaned

copper substrates are shown in Fig5 (A, B, C and D). It is clear that deposits prepared by immersion cleaning the copper in the electropolishing solution resulted in the retention of the original aligned deformed surface, which can be seen from Fig5C and 5D. It can be clearly seen that electropolishing removes this effect and this can be seen by comparing the higher magnification SEMs Fig5A and 5B. These micrographs clearly reveal the highly significant difference in the substrate surface which was obtained by simply immersion cleaning as compared to electro-polishing for 2 minutes. On the basis of these results it was anticipated that the further addition of aligned deformation marks to the surface of the as manufactured Cu foil could contribute to enhanced deposits in terms of electrode properties. When further directional deformation was added to the Cu foil substrate using 1200 grade sandpaper, it can be seen that highly significant improvements are achieved in the discharge capacity alongside a constant cycle life capability. This performance was verified by reproduction of the exact experimental conditions and the results were found to be similar as can be seen from Fig4. These results clearly demonstrate the importance of directional high energy surface roughness being generated on the Cu foil substrate as the discharge capacity has increased from around 350mAh/g to around 600mAh/g with corresponding constant cycle life capability. The theoretical discharge capacity for the alloy deposit with 62wt% of Sn in the alloy gives a value of 614mAh/g and as can be seen in Fig4, a discharge capacity of 600mAh/g was achieved, which is almost equal to the theoretical capacity of the Sn content of the alloy combined with an extremely good cycle life.

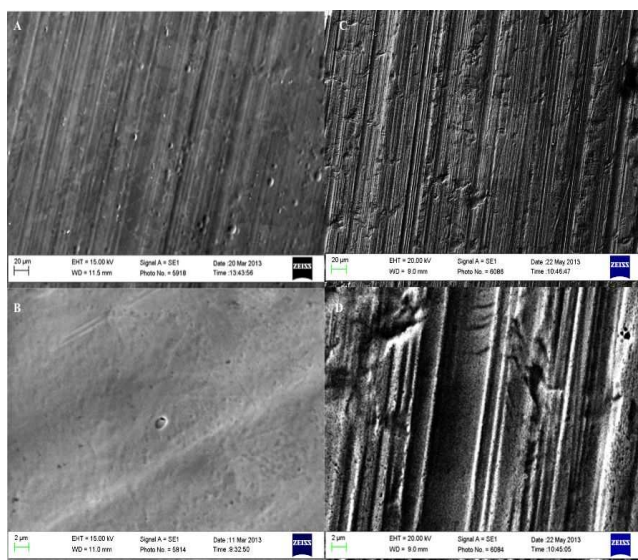


Figure 5. Surface morphology of the electropolished (A & B) and only immersed (C & D) copper substrate using SEM.

The earlier published results [20] which were obtained using an alloy deposit with 82wt% of Sn gave excellent electrode properties with a Cu substrate exhibiting directional deformation deriving from the manufacturing process. While this result was a useful indicator of the importance of the

surface condition of the Cu foil substrate, it is to be expected that the manufactured foil could vary in surface roughness deformation from batch to batch and possibly within a batch, thus the resulting deposits could vary in electrode properties according to the levels of micro-deformation. The results obtained using immersion in the polishing solution to clean the substrate followed by controlled surface deformation show that the surface deformation condition of the substrate is critical in relation to the type of morphology grown by electrodeposition to form a deposit which supports delivery of a discharge capacity which is near to the theoretical capacity for the Sn content of the alloy alongside supporting the ability to give a constant cycle life.

4. Conclusions

- A range of novel amorphous Sn-Ni-Fe alloys were successfully deposited using a pulse plating process with various t_{on}/t_{off} pulse time ratios and peak currents.
- The pulse plated Sn-Ni-Fe alloys exhibiting a pronounced spherical/nodular grain structure show distinct potential to provide a new electrodeposited anode material for application in the Li ion battery. The capacity performance, charging efficiency and the cycle life obtained gave improved results to carbon anodes which are the main material being used at present for Li-Ion battery application.
- The results show that the surface condition of the substrate plays a fundamental role in the nature of the subsequent surface morphology developed during pulse electrodeposition and subsequently fundamentally affects the performance of the electrodeposited electrode in the Li-ion battery cell in terms of acceptable discharge capacity and cycle life.
- Further more detailed studies are now needed to produce controlled amounts of directional surface deformation similar to that found on the surface of the as manufactured Cu foil substrates to achieve alloy electrodeposits with carefully controlled surface morphologies which support discharge capacities near to the theoretical capacity for the Sn content of the alloys deposited alongside achieving a constant cycle life.

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